



Short Communication

## Mediated reduction of oxygen at poly(phenosafranine) modified electrodes

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### 1. Introduction

The immobilization of catalytic molecules on electrodes is advantageous due to their ready separation from the solution medium and the small amount of catalyst necessary for the reaction [1–4]. Different methods are available to immobilize catalysts on electrode surfaces. The most frequently used method is the adsorption of catalytic molecules on a polyelectrolyte or clay or zeolite film coated electrode [1, 3, 4]. Another method is the immobilization of catalysts through electropolymerization of monomers on the surface [1, 5]. This type of electrode modification allows the electrocatalyst to be dispersed at the molecular level with good activity towards many electrocatalytic reactions [1, 2, 5, 6].

Electrocatalytic reduction of dioxygen has been studied extensively because of its relevance to fuel cell technology [7]. Dioxygen reduction to hydrogen peroxide is a two-electron reaction and the four-electron reduction leads to the formation of water [8]. The kinetics and mechanisms of oxygen reduction have been investigated using a wide range of cathode materials and electrolytes [9–13]. In this work phenosafranine ( $PS^+$ ) (Figure 1(a)), a phenazine dye, was electropolymerized on a basal plane graphite (BPG) electrode and zeolite-L coated BPG electrode to give poly(phenosafranine) (BPG/poly(phenosafranine)) and zeolite–poly(phenosafranine) (BPG/zeolite-L/poly(phenosafranine)) modified electrodes. The oxygen electroreduction was then studied at such electrodes in 0.1 M  $NaH_2PO_4$ .

### 2. Experimental details

Zeolite-L (Tosoh Co.) was purified to remove the  $Fe^{2+}$  impurity by stirring the zeolites in 1 M KCl [14]. Phenosafranine (Wako Pure Chemicals) was purified according to the reported procedure [15]. All other chemicals were of analytical grade and used as received. To prepare the zeolite coated electrode, 0.5% zeolite-L colloid with 0.01% of poly(vinyl alcohol) (as a binder) was prepared and a 15  $\mu$ l of the aliquot was transferred onto a 0.21  $cm^2$  of BPG electrode and air dried

(represented as BPG/zeolite-L). These modified electrodes were used to electropolymerize  $PS^+$  on the zeolite coating. Cyclic voltammograms were recorded using an EG&G PAR 273A potentiostat/galvanostat equipped with a RE 0151 recorder. A three electrode cell with poly(phenosafranine) or zeolite–poly(phenosafranine) modified BPG electrode as working electrode, a 1  $cm^2$  platinum plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode were used. The rotating disc electrode (RDE) experiments were done with an EG&G PARC model 616 rotating disc electrode setup with glassy carbon (GC) modified with poly(phenosafranine) or zeolite–poly(phenosafranine) as working electrode, platinum wire as counter electrode and silver/silver chloride as reference electrode. All the experiments were carried out under nitrogen and/or oxygen saturated conditions. Hydrogen peroxide was estimated by iodometric and spectrophotometric methods [16, 17].

### 3. Results and discussion

A poly(phenosafranine) modified electrode (represented as BPG/poly(phenosafranine)) was prepared by the oxidative polymerization of  $PS^+$  ( $5 \times 10^{-4}$  M) in 0.05 M  $H_2SO_4$  by cycling the potential between –0.5 and 1.3 V [2]. To prepare a zeolite–poly(phenosafranine) composite electrode, the zeolite coated electrode (BPG/zeolite-L) was dipped in a cell solution containing  $5 \times 10^{-4}$  M phenosafranine and 0.2 M  $NaClO_4$  in 50:50 acetonitrile:water mixture. Potential cycling between –1.0 and 1.2 V yielded the zeolite–poly(phenosafranine) coated electrode (BPG/zeolite-L/poly(phenosafranine)) [2].  $PS^+$  shows a pair of peaks corresponding to the two-electron reduction of  $PS^+$  to  $PSH_2^+$  (leuco-phenosafranine) in the potential sweep between 0.4 and –1.0 V (Equation 1).



When the anodic sweep limit was extended to 1.3 V, a shoulder wave appeared around 1.2 V due to the

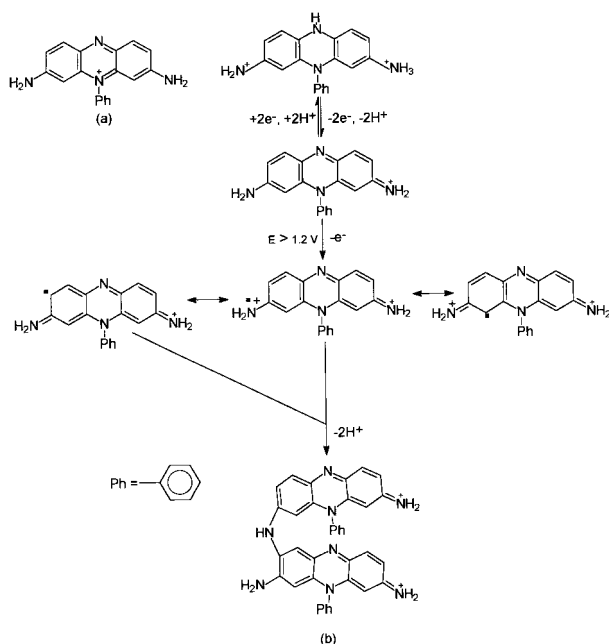


Fig. 1. (a) Structure of phenosafranine. (b) Proposed phenosafranine coupling scheme.

formation of phenosafranine radical cation (Figure 1) [18]. The oxidation current observed at 1.2 V declines in apparent size in the first few sweeps. On removal of the electrode from the  $PS^+$  containing solution, a red coloured film was observed on the surface of the electrode. Such modified electrodes were kept in distilled water for 30 min and in the supporting electrolyte solution for one hour before the experiments. It is proposed that the primary step in the poly(phenosafranine) film formation is the one-electron oxidation of monomer  $PS^+$  to form a radical cation [18]. Delocalization in the radical cation is represented in several canonical forms (Figure 1). Radical dimerization can

occur via carbon-nitrogen coupling route [18, 19]. An insoluble, oligomeric, probably cross-linked film is gradually produced. This poly(phenosafranine) film is electroactive because each monomer unit retains its electroactive heterocyclic nitrogen atom. Moreover, as polymerization occurs, more pendent amine groups become nitrogen bridges and these bridges become electroactive similar to those in polyaniline and poly(thiophene) films [18].

The poly(phenosafranine) modified electrodes showed a broad peak in 0.1 M  $NaH_2PO_4$  in the absence of oxygen (Figure 2A(a) and 2B(a)). The electrochemical data for the modified electrodes are summarized in Table 1. Even though the  $I_{pa}/I_{pc}$  ratio of the two electrodes are almost same, the lower  $\Delta E_p$  values observed (Table 1) at zeolite coated electrode suggest that the reversibility of the catalyst is improved and the poly(phenosafranine) film becomes more permeable. The intrazeolitic electron transfer is not occurring in the case of ship-in-a-bottle complexes [20, 21]. In the present case, the poly(phenosafranine) film formed in the channels of zeolite-L, on the surface of the zeolite, and/or in the interlayer region of the zeolite particles is electroactive.

The cyclic voltammograms of the modified electrodes recorded in the absence and presence of oxygen in 0.1 M  $NaH_2PO_4$  are shown in Figure 2. In the absence of oxygen, a redox wave due to the reduction and reoxidation of the  $PS^+$  species in the poly(phenosafranine) film is observed (Equation 1). In the absence of oxygen, the  $E_{1/2}$  value of BPG/zeolite-L/poly(phenosafranine) shows a small negative shift when compared to the BPG/poly(phenosafranine) electrode (Table 1). This indicates the less favoured reduction of  $PS^+$  in the presence of zeolite. A similar shift in the  $E_{1/2}$  value was reported for monomer  $PS^+$  [22] in Nafion<sup>®</sup> film. In the presence of oxygen, the reduction current is increased

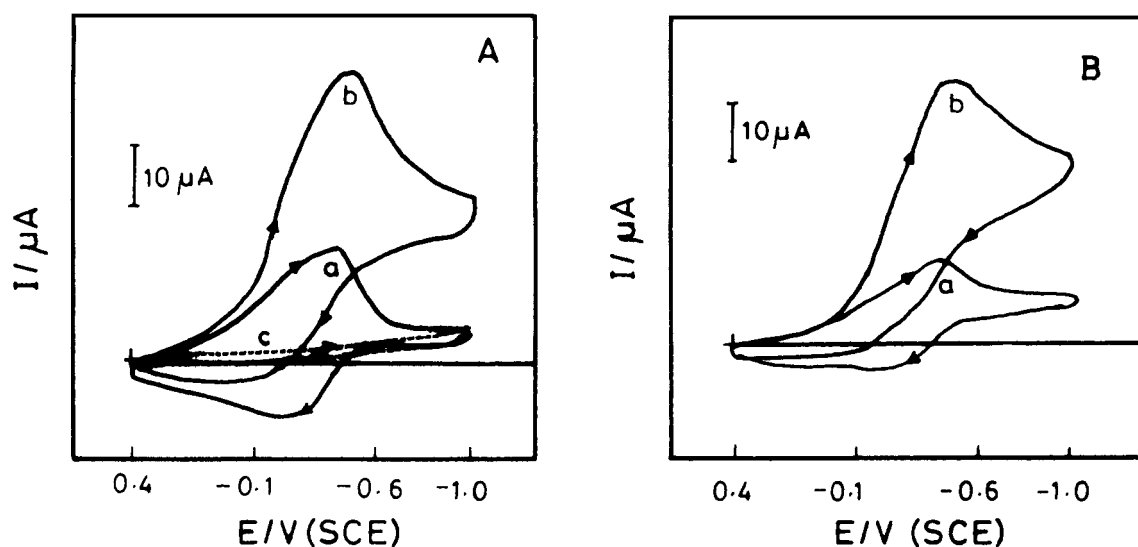
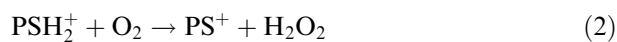


Fig. 2. (A) Cyclic voltammograms of BPG/poly(phenosafranine) (a, b) and BPG (c) electrodes in the absence (a, c) and presence (b) of oxygen in 0.1 M  $NaH_2PO_4$ . (B) Cyclic voltammograms of BPG/zeolite-L/poly(phenosafranine) electrodes in the absence (a) and presence (b) of oxygen in 0.1 M  $NaH_2PO_4$ .

Table 1. Electrochemical data of the poly(phenosafranine) modified electrodes in 0.1 M NaH<sub>2</sub>PO<sub>4</sub> at a scan rate of 20 mV s<sup>-1</sup>

Electrode	$E_{1/2}/V$	$\Delta E_p/mV$	O <sub>2</sub> reduction potential/V	$I_{pa}/I_{pc}$
BPG	—	—	-0.75	—
BPG/poly(phenosafranine)	-0.34	230	-0.48	0.70
BPG/zeolite-L/poly(phenosafranine)	-0.38	150	-0.45	0.73

due to the catalytic reduction of oxygen by the reduced PS<sup>+</sup> (PSH<sub>2</sub><sup>+</sup>) to H<sub>2</sub>O<sub>2</sub> (Equation 2).



The oxygen reduction potential is positively shifted by 300 mV at the BPG/zeolite-L/poly(phenosafranine) electrode and 270 mV at the BPG/poly(phenosafranine) electrode when compared to bare BPG (Table 1). The BPG/zeolite-L/poly(phenosafranine) electrode showed higher amounts of H<sub>2</sub>O<sub>2</sub> and turnover numbers when compared to the BPG/poly(phenosafranine) electrode. At an applied potential of -0.5 V vs SCE for 30 min in the presence of oxygen, the BPG/poly(phenosafranine) electrode produced 0.19 μmol H<sub>2</sub>O<sub>2</sub> (turnover number: 189, percentage of formation of H<sub>2</sub>O<sub>2</sub>: 62%) whereas, the BPG/zeolite-L/poly(phenosafranine) electrode produced 0.24 μmol H<sub>2</sub>O<sub>2</sub> (turnover number: 348, percentage of formation of H<sub>2</sub>O<sub>2</sub>: 71%). Thus the presence of zeolite-L increases the turnover numbers and the percentage formation of H<sub>2</sub>O<sub>2</sub>. Zeolites are known to concentrate oxygen inside their cages and channels [23, 24]. The increase in the concentration of oxygen at the catalytic site zeolite-phenosafranine composite film, leads to the increase in the amounts of H<sub>2</sub>O<sub>2</sub> and turnover number of PS<sup>+</sup>. These observations show that

the BPG/zeolite-L/poly(phenosafranine) electrode is comparatively more stable and efficient than the BPG/poly(phenosafranine) film.

The cyclic voltammograms recorded for these modified electrodes in the absence of oxygen, both before and after one hour of oxygen reduction, showed 20–30% decreases in peak currents. The decrease in the peak current may be due to the loss of poly(phenosafranine) in the presence of oxygen. Similar loss of naphthoquinone catalyst (~50%) was reported in the mediated electrochemical reduction of oxygen [6]. The  $I_{pa}/I_{pc}$  ratio observed in the absence of oxygen for the modified electrodes is the same before and after oxygen reduction. This indicates that the redox properties of the remaining poly(phenosafranine) is not affected by oxygen reduction. Figure 3 shows the current-potential curves under steady state conditions and the plot of applied potential against the amounts of H<sub>2</sub>O<sub>2</sub> produced for the modified electrodes. The H<sub>2</sub>O<sub>2</sub> formation is observed from -0.1 V onwards. This means that the reduced PSH<sub>2</sub><sup>+</sup> mediated the reduction of O<sub>2</sub> to produce H<sub>2</sub>O<sub>2</sub>.

To investigate the electron transfer kinetics at these modified electrodes, the current-potential curves were recorded for the reduction of dioxygen at a rotating

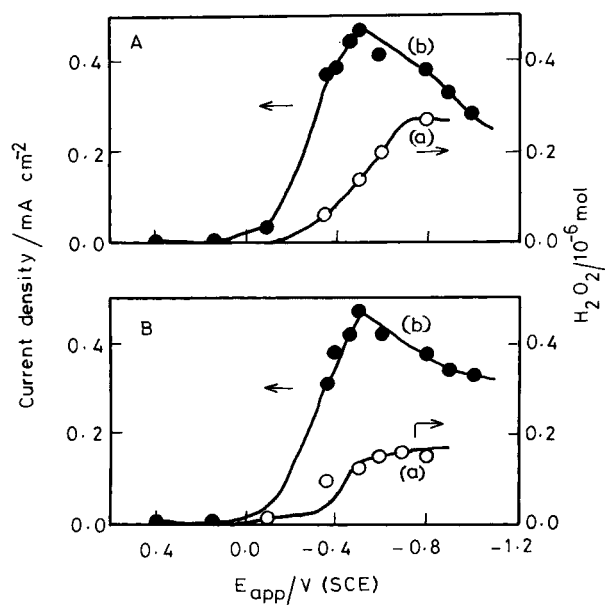


Fig. 3. The plot of current density against potential (a) and the dependence of applied potential on the formation of H<sub>2</sub>O<sub>2</sub> (b) at BPG/poly(phenosafranine) (A) and BPG/zeolite-L/poly(phenosafranine) (B) electrodes (electroactive species (Γ) at BPG/poly(phenosafranine) is  $2.02 \times 10^{-9}$  mol cm<sup>-2</sup> and at BPG/Zeolite-L/poly(phenosafranine) is  $8.29 \times 10^{-10}$  mol cm<sup>-2</sup>).

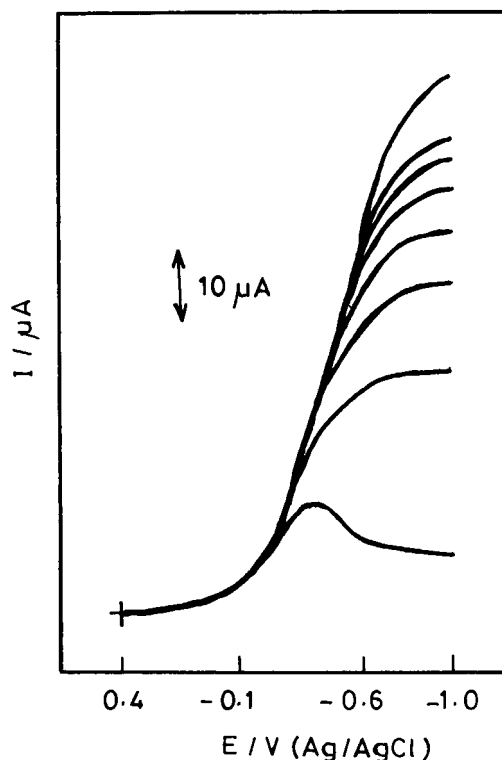


Fig. 4. Current-potential curves for GC/poly(phenosafranine) electrode (rotation rate 0, 100, 200, 300, 400, 500, 600 and 900 rpm).

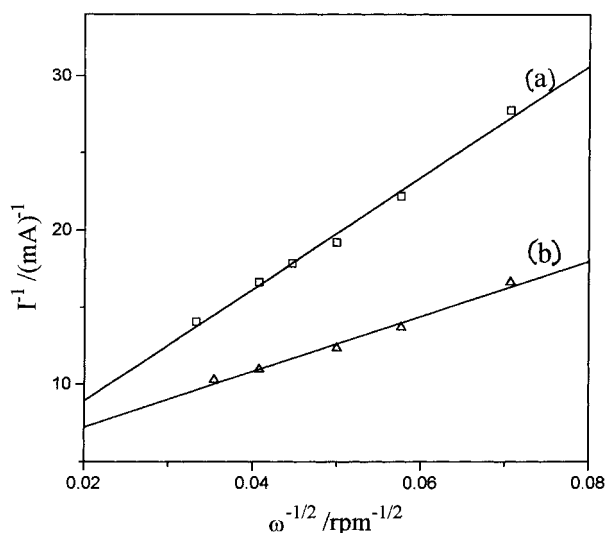


Fig. 5. Koutecky–Levich plots for GC/poly(phenosafranine) (a) and GC/zeolite-L/poly(phenosafranine) (b) electrodes.

glassy carbon disc electrode modified with poly(phenosafranine) in 0.1 M  $\text{NaH}_2\text{PO}_4$ . A representative of the current–potential curves for the GC/poly(phenosafranine) electrode is shown in Figure 4. The GC/zeolite-L/poly(phenosafranine) electrode also show very similar results. The Levich plots [25] of limiting current against (rotation rate) $^{1/2}$  shows a deviation from the linearity (Figure not shown) indicating that a chemical reaction takes place after the reduction of  $\text{PS}^+$  in the film (Equation 2) [12]. The  $k$  (rate constant governing the reaction of the catalyst with oxygen) values evaluated from the intercept of Koutecky–Levich plot (Figure 5) [26] is higher for the GC/zeolite-L/poly(phenosafranine) electrode ( $5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) than the GC/poly(phenosafranine) electrode ( $3.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ). The  $k$  values observed for the poly(phenosafranine) system is one order of magnitude lower than the reported  $k$  values ( $9.8\text{--}14 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) for the electrocatalytic reduction of dioxygen by cobalt(II) porphyrin adsorbed on BPG electrode [12].

The BPG/poly(phenosafranine) and BPG/zeolite-L/poly(phenosafranine) electrodes are prepared and used for catalytic reduction of oxygen. The zeolite-L modified electrode improves the reversibility of the poly(phenosafranine) catalyst. Zeolite-L enhances the poly(phenosafranine) mediated oxygen reduction process at the modified electrodes.

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